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MECHANISM OF MONURON-ACCELERATED DICYANDIAMIDE CURE OF EPOXY RESINS

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POLYMER RESEARCH DIVISION

July 1981

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ABSTRACT

A very interesting and practical property of trisubstituted ureas such as Monuron, N-(4-chlorophenyl)-N',N'-dimethylurea, is the ability of this class of aryl ureas to accelerate the dicyandiamide (Dicy) cure of epoxy resins. Earlier workers had proposed that the *in situ* formation of dimethylamine from Monuron was an important factor in explaining the mechanism of the Monuron-accelerated dicyandiamide cure of epoxy resins. The main source of dimethylamine did not appear to us to be that which had been previously described. We have found that the amine is generated by a cyclocondensation reaction between the aryl urea and the resin to form a 2-oxazolidone.

During this study, it was found that the effectiveness with which dimethylamine activates Dicy, especially when compared to other materials such as trimethylamine, made this amine unique. It is postulated that dimethylamine has a strong proclivity to remove a proton from Dicy, thereby creating a highly active nucleophilic species. This enhancement of the nucleophilic nature of the hardening agent (Dicy) would account for the increased reactivity of Dicy toward epoxy resins.

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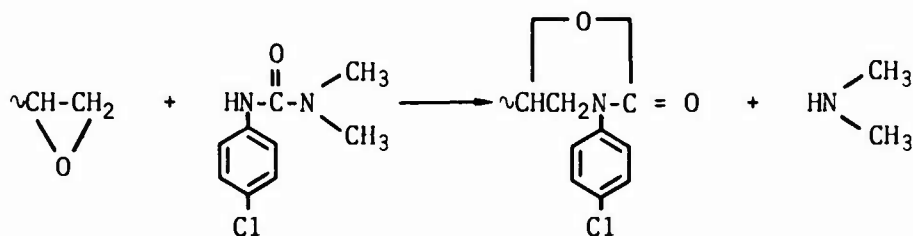
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INTRODUCTION

The earlier workers, P. N. Son and C. D. Weber,¹ reported that the *in situ* formation of dimethylamine from the aryl urea Monuron, N-(4-chlorophenyl)-N',N'-dimethylurea, was an important factor in the mechanism of the Monuron-accelerated dicyandiamide (Dicy) cure of epoxy resins.

A study¹ was made to determine the effectiveness of Monuron as an accelerator using differential scanning calorimetry (DSC) at a heating rate of 10°C/min and a synergistic effect between Monuron and Dicy was observed. The significance of the reaction between the epoxy resin and Monuron was not considered by these investigators. In search of a low temperature source of dimethylamine, they reported that Monuron and Dicy, when heated at 112°C to 118°C in bis(2-methoxyethyl)ether (bp 162°C), yielded 35.5% of a linear compound, 1-cyano-3-(p-chlorocarbanilino)guanidine. A reexamination² in our laboratory revealed that the main source of dimethylamine is very likely not this reaction. We were unable to prepare the linear compound at 112°C to 118°C, and at 162°C a cyclic isomer was realized.

Initially, we restricted our effort to find a pathway to dimethylamine to reactions in which epoxy-containing compounds were present. It was found that the main source of dimethylamine stems from a low temperature cyclocondensation reaction between the oxirane ring and the aryl urea accelerator² to form a 2-oxazolidone.* This reaction is indicated by the oxirane ring and Monuron below:



RESULTS AND DISCUSSION

The effectiveness of the trisubstituted ureas as accelerators was illustrated with DSC.² With a heating rate of 2°C/min, a mixture of Diuron, N-(3,4-dichlorophenyl)-N',N'-dimethylurea, and tetraglycidyl methylene dianiline (TGMDA) displayed an exotherm at 129°C. The three-component system consisting of Diuron, TGMDA, and Dicy also yielded an exotherm at 129°C. In contrast, the two-component TGMDA-Dicy mixture produced an exotherm at 170°C. The examination of the above mixtures made us aware of the thermal relationship between the two- and three-component systems. In other words, the resin-accelerator reaction had activated the Dicy so that curing occurred at a lower temperature.

The thermal relationship was further investigated with the monofunctional epoxide, phenyl glycidyl ether (PGE). This epoxide was used to magnify the reaction temperature

*LaLIBERTE, B. R. *The Reaction of Diuron with Epoxy Groups*. Army Materials and Mechanics Research Center, AMMRC TN 79-1, January 1979, and other work by LaLiberte and Bornstein, manuscript in preparation.

1. SON, F. N., and WEBER, C. D. *Some Aspects of Monuron-Accelerated Dicyandiamide Cure of Epoxy Resins*. J. Applied Polymer Science, v. 17, 1973, p. 1305-1313.

2. LaLIBERTE, B. R., SACHER, R. E., and BORNSTEIN, J. *Acceleration of the Epoxy Resin-Dicyandiamide Cure Cycle by Trisubstituted Ureas*. Army Materials and Mechanics Research Center, AMMRC TR 81-30, June 1981.

differences of Monuron (mp 172°C) and Diuron (mp 154°C). Diuron and Monuron were each intimately mixed with PGE in equimolar amounts to form two-component mixtures. Three-component systems were formulated on the basis of five moles of PGE, one mole of the urea accelerator, and four moles of Dicy. The exothermic reaction temperatures of the two- and three-component systems, recorded (DSC) at 2°C/min, are:

PGE + Diuron:	129°C	PGE + Monuron:	148°C
PGE + Diuron/Dicy:	128°C	PGE + Monuron/Dicy:	130°C

The results from the Diuron-PGE study supported the previously found relationship that the exothermic reaction temperature of the three-component system was about the same as that of the epoxy-aryl urea reaction. Interestingly, the three-component systems have about the same reaction temperature. Thus Monuron at a heating rate of 2°C/min generated dimethylamine in sufficient amounts to activate Dicy so that chemical reaction of the epoxide took place at 130°C.

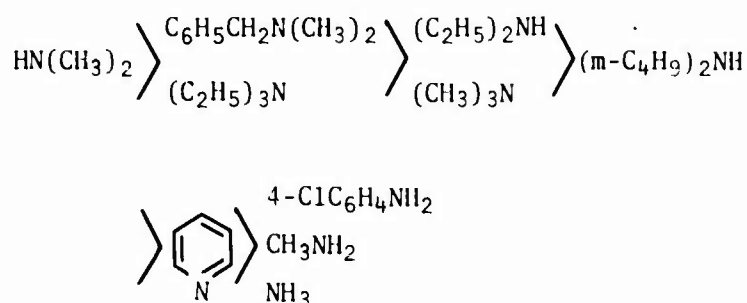
The above observations prompted further study. Accordingly, the investigation was extended to include a nonchlorinated low-melting aryl urea Nonuron, N-phenyl-N',N'-dimethylurea (mp 134°C). The reaction temperatures of the aryl ureas were determined with a different epoxy-containing substrate, p-tertiary butylphenyl glycidyl ether (PTBGE). Reaction temperatures were first measured (DSC) at 2°C/min and then at the extremely slow heating rate of 0.5°C/min.

	Reaction Temperatures, deg C	
	Heating Rate per minute	
	2°C	0.5°C
PTBGE + Nonuron	161	128
+ Nonuron/Dicy	-	116
+ Diuron	148	116
+ Diuron/Dicy	-	113
+ Monuron	158	118
+ Monuron/Dicy	-	114

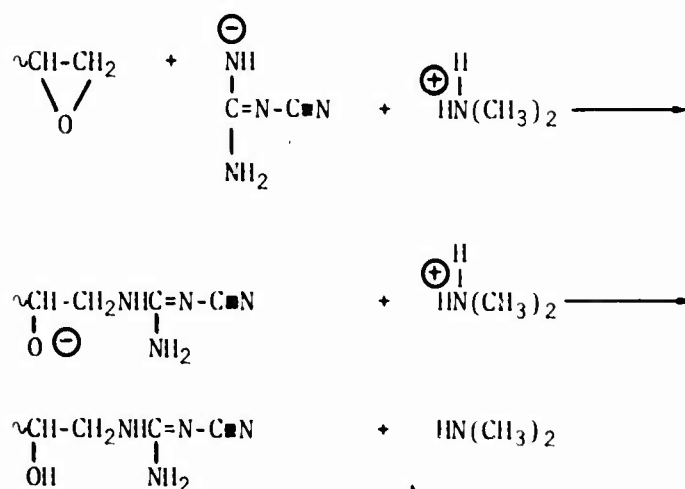
The heating rate of 0.5°C/min produced results that were extremely informative. Regardless of the accelerator, all three-component systems had approximately the same reaction temperature and this fact is an indication that activation of Dicy may be more dependent on the formation of an active species of Dicy rather than the rate at which dimethylamine was generated. Son and Weber's demonstration of the synergistic effect of Monuron and Dicy on the cure temperature was illustrated by comparing the resin - Dicy temperature to that of the three-component system. This comparison is a reality that is well known in the state of the art.

In a search for an active species of Dicy, we attempted to react dimethylamine (bp 6°C) and Dicy at 0°C. For all practical purposes, the infrared analysis and the melting point determination of the treated Dicy indicated that no chemical reaction had taken place. This Dicy was mixed with an epoxy resin and examination of this mixture (DSC) at 2°C/min very surprisingly afforded an exotherm at 150°C. In contrast, untreated Dicy produced an exotherm with the resin at 179°C. Partial activation may have been realized but further study is indicated.

Tertiary amines, such as N,N-dimethylbenzylamine, have been reported by Saunders, Levy, and Serino³ to catalyze Dicy. It is interesting that N,N-dimethylbenzylamine is similar to dimethylamine in that it contains the dimethylamino group and that both these amines are able to activate Dicy. It was found, in contrast, that the diethylamino derivatives of the aryl ureas, such as N-phenyl-N',N'-diethylurea and N-(4-chlorophenyl)-N',N'-diethylurea, demonstrated limited ability to activate Dicy. It should be pointed out that on the basis of basicity and steric hindrance, it would be expected that the difference in the activation of Dicy by dimethylamine or diethylamine should be marginal. Consequently, dimethylamine was considered to be a unique amine. This belief led to an investigation in which the activating effect of a number of amines was studied. As a result of this work amines may now be arranged in a series according to their decreasing ability to activate Dicy.



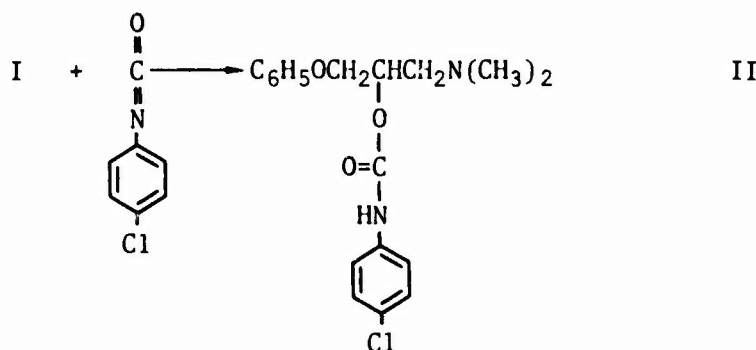
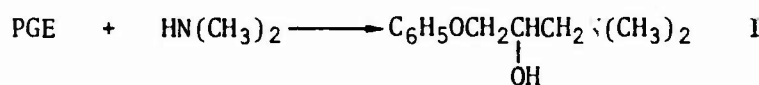
As can be seen, dimethylamine is a better activator than trimethylamine. A feasible explanation of the the dominant position of dimethylamine in the activation series may be ascribed to a delicate balance between basicity, nucleophilicity, steric hindrance, and diffusion. On the basis of this activation series, we wish to propose that dimethylamine removes a proton from Dicy, thereby generating a reactive nucleophilic species. This enhancement of the nucleophilic nature of the hardening agent (Dicy) would account for the increased reactivity of Dicy toward epoxy resins.



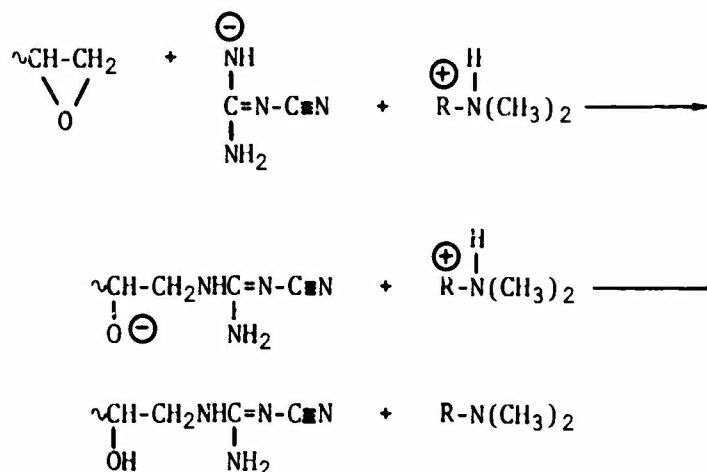
3. SAUNDERS, T. F., LEVY, M. F., and SERINO, J. F. *Mechanism of the Tertiary Amine-Catalyzed Dicyandiamide Cure of Epoxy Resins*. J. Polymer Science, A-1, v. 5, 1967, p. 1609-1617.

It was of interest to determine the relationship between the structure of the trisubstituted ureas and their ability to effect the activation of Dicy. Tetramethylurea and 1,3-bis(4-chlorophenyl)urea were found not to possess any accelerative property. It was observed that 1,1-dimethylurea was not as good an accelerator as the aryl ureas; however, it was found that this compound was definitely more effective than 1,3-dimethylurea. It appears then that for a urea to be a useful accelerator it must contain an aryl substitute as well as the gem-dimethyl moiety.

The mechanism proposed above failed to take into consideration the ability of dimethylamine to open the epoxy functionality of the substrate to form tertiary amines. This prompted the preparation of two compounds (I and II) from the reactants, phenyl glycidyl ether (PGE), dimethylamine, and 4-chlorophenyl isocyanate as indicated below:



Compounds I and II were found to have excellent accelerative properties. The ease with which dimethylamine opened the oxirane ring to form the compound I necessitated the consideration of a second and more general mechanism whereby the proton acceptor dimethylamine was replaced by $\text{R-N}(\text{CH}_3)_2$ in explaining the process of Dicy activation.



Where R is equal to H, the proton acceptor is dimethylamine. R may represent other groups which would be present in substances obtained by the attack of dimethylamine on the epoxy functionality. The foregoing mechanism is now flexible enough to encompass some of the various elements which may contribute to the overall activation of Dicy.

EXPERIMENTAL

Differential scanning calorimetric experiments were conducted in open aluminum pans on a DuPont 990 thermal analyzer with a 902 DSC plug-in module in a static atmosphere. The exothermic reaction temperatures were taken at the apex of the heating curves.

Preparation of Compounds I and II

Phenyl glycidyl ether was reacted with an excess of dimethylamine at 0°C to form compound I, 1-phenoxy-3-dimethylamino 2-propanol. Compound I and p-chlorophenyl isocyanate were reacted to yield the carbamate II.* The elemental analysis of the previously unreported carbamate derivative II is shown.

Calcd for: $C_{18}H_{21}ClN_2O_3$; C, 62.07; H, 6.08; Cl, 10.18; N, 8.04%

Found: C, 61.90; H, 6.12; Cl 10.38; N, 7.98%.

ACKNOWLEDGMENT

Dr. C. A. Byrne kindly prepared compounds I and II for this study.

*The detailed preparation of this material will be reported by Dr. C. A. Byrne.

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